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APPROVAL SHEET

Title of Dissertation: **Needle Trap Sampling with Gas Chromatography Analysis to Determine Short Term Exposure Limit and Ceiling Concentrations for Selected Organic Vapors**

Name of Candidate: **CPT Simon J. Strating**, Master of Science in Public Health

THESIS AND ABSTRACT APPROVED:

DATE:

March 30, 2012

Duvel W. White, LTC, Ph.D.
DEPARTMENT OF PREVENTIVE MEDICINE & BIOMETRICS
UNIFORMED SERVICES UNIVERSITY OF THE HEALTH SCIENCES
Committee Chairperson & Thesis Advisor

March 30, 2012

Philip A. Smith, Ph.D.
HEALTH RESPONSE TEAM – SALT LAKE TECHNICAL CENTER
OCCUPATIONAL SAFETY & HEALTH ADMINISTRATION (OSHA)
Committee Member

March 30, 2012

Roger L. Gibson, DVM, MPH, Ph.D.
DEPARTMENT OF PREVENTIVE MEDICINE & BIOMETRICS
UNIFORMED SERVICES UNIVERSITY OF THE HEALTH SCIENCES
Committee Member

March 30, 2012

Michael E. Stevens Jr., LCDR, Ph.D.
DEPARTMENT OF PREVENTIVE MEDICINE & BIOMETRICS
UNIFORMED SERVICES UNIVERSITY OF THE HEALTH SCIENCES
Committee Member

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***“NEEDLE TRAP SAMPLING WITH GAS CHROMATOGRAPHY ANALYSIS TO
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FOR SELECTED ORGANIC VAPORS”***

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Simon J. Strating
CPT, MS, U.S. Army
Preventive Medicine & Biometrics
Uniformed Services University
10 April 2012

ABSTRACT

Title of Thesis: *"NEEDLE TRAP SAMPLING WITH GAS CHROMATOGRAPHY ANALYSIS TO DETERMINE SHORT TERM EXPOSURE LIMIT AND CEILING CONCENTRATIONS FOR SELECTED ORGANIC VAPORS"*

Author: CPT Simon J. Strating
Masters of Science in Public Health, 2012
Uniformed Services University of the Health Sciences

Thesis Advisor: LTC Duvel W. White
Assistant Professor
Department of Preventive Medicine and Biometrics

A needle trap device (NTD) was used for rapid (60 s) quantitative sampling of short term exposure limit (STEL) and ceiling (C) concentrations using a manually operated pump to collect small volume (10 ml) vapor samples of methylene chloride, benzene, toluene, and tetrachloroethylene. Solventless introduction of chemical samples for gas chromatography (GC) analysis with flame ionization detection (FID) yielded linear results ($>0.99 R^2$) for vapor standard mixtures of the four target analytes ranging from 10% to 200% of their respective STEL and C concentrations. The NTDs showed storage stability ($>86\%$ recovery) at room temperature over a 14-day test period. Due to the brief sampling period and the avoidance of solvent dilution, the use of NTDs for STEL/C measurements can allow industrial hygienists to collect occupational and environmental samples that reflect a nearly instantaneous exposure concentration.

TITLE PAGE

***NEEDLE TRAP SAMPLING WITH GAS CHROMATOGRAPHY ANALYSIS TO
DETERMINE SHORT TERM EXPOSURE LIMIT AND CEILING CONCENTRATIONS
FOR SELECTED ORGANIC VAPORS***

by

Captain Simon J. Strating

Environmental Science and Engineering Officer

United States Army

A thesis submitted to the Faculty of the Department of Preventive Medicine and
Biometrics Graduate Program of the Uniformed Services University of the Health

Sciences in partial fulfillment of the requirements for the degree

of

MASTERS OF SCIENCE IN PUBLIC HEALTH, 2006

DEDICATION

I dedicate this master's thesis to my wife, Eve and my daughters, Kyla and Kimberly. I could not have completed this work without your support and understanding. Thank you for the sacrifices you have endured throughout my Army career.

-Simon

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CHAPTER ONE: INTRODUCTION

STATEMENT OF PROBLEM

A need exists to measure nearly instantaneous vapor concentrations for a number of airborne industrial hygiene chemical stressors (hazardous chemical substances) because many current methods rely on time weighted average (TWA) samples that are not rapid enough to comply with regulatory guidance. Several types of permissible exposure limit (PEL) standards other than the frequently used eight-hour TWA standard have been promulgated by the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA). These include the short term exposure limit (STEL) and ceiling (C) standards. A C standard represents a level of exposure that should never be exceeded, whereas an exposure greater than a TWA STEL standard averaged over 15 min is also unacceptable.⁽¹⁾ Both the C and STEL standards are based on acute toxicity. Four airborne industrial hygiene chemical stressors chosen for this study are: benzene and methylene chloride for which STEL standards apply, and tetrachloroethylene and toluene for which C standards apply.

Current methods for evaluating C or STEL compliance rely on either quantitative handheld sensors, or a developed sampling and analytical method that usually relies on sorbent tube sampling with solvent desorption and analysis by gas chromatography (GC). Benzene, methylene chloride, tetrachloroethylene, and toluene samples for STEL or C compliance are all currently collected on a charcoal tube to determine 15 min TWA concentrations following GC analysis with a flame ionization detector (GC/FID).⁽²⁻⁵⁾

Analysis following solvent desorption must take into account dilution by the solvent, which reduces GC/FID sensitivity for the chemical of interest. Thus, a 15 min TWA sample is collected for C standard analytes (e.g. for tetrachloroethylene and toluene) even though the information needed is the instantaneous sample concentration.

BACKGROUND/LITERATURE REVIEW

Solid Phase Microextraction (SPME)

The pace of research on sampling methods using small sorbent volumes has increased since the early 1990s when solid phase microextraction (SPME) was first described.⁽⁶⁾ "Microextraction is defined as an extraction technique where the volume of the extracting phase is very small in relation to the volume of the sample, and extraction of analytes is not exhaustive. In many cases only a small fraction of the initial analyte is extracted for analysis."⁽⁷⁾ The SPME technique is usually employed for passive sampling, where analytes in the system being sampled passively diffuse into a thin layer of polymer material coated over a small fused silica fiber. Eventually, equilibrium may be attained between the coating material and the system being sampled where no further net analyte uptake occurs. With SPME, the overall analyte concentration in the system being sampled is not appreciably changed due to the small scale of extraction.

The advantages of SPME in the field are rapid sample preparation with the integration of sampling, extraction, concentration, and sample introduction into a single step;⁽⁸⁾ and its portability, simplicity, sensitivity, and broad applicability for qualitative field samples.⁽⁹⁾ These advantages have made SPME a popular field sampling method

and led to many commercially available products. The disadvantages to SPME include the difficulty in achieving quantitative results from field sampling due to the need for calibration curves conducted in the same environmental conditions as the field samples⁽¹⁰⁾ and competitive displacement of low affinity VOCs in the sample matrix.⁽¹¹⁾ Several recent scientific advances have made SPME field sampling easier to calibrate but do not remove the need for a calibration curve, and include FLEC® cell SPME,^(12, 13) carbon nanotube-coated SPME,⁽¹⁴⁾ and cold fiber SPME.⁽¹⁵⁾

Fick's law quantitative SPME

Advances in field sampling with TWA diffusion have shown that fiber-retracted SPME devices can be used for quantitative analysis with a simplified calibration using Fick's first law of diffusion, shown in Figure 1.^(16, 17) This method eliminates the need for a calibration curve or internal standard, and the sampling rate is independent of face velocity making it ideal for field environments.⁽¹⁸⁾ In 2004, Chen *et al.* developed a fiber-retracted SPME sampler that could quantitate toluene in 5 min⁽¹⁹⁾ and in 2006 he demonstrated his sampler could quantitate a 15 min STEL for methylene chloride.⁽²⁰⁾ Although the 15 min STEL for methylene chloride is promising, the 5 min collection of toluene does not address the OSHA instantaneous requirement for C measurement. Additionally, most of the research on fiber-retracted SPME has involved longer sampling times: volatile organic compounds (90 min – 7 days);⁽²¹⁾ C5-C15 n-alkanes (120-210 min);⁽²²⁾ hydrocarbons and formaldehyde (15 min – 16 h);⁽²³⁾ and volatile sulfur compounds (2-12 h).⁽²⁴⁾

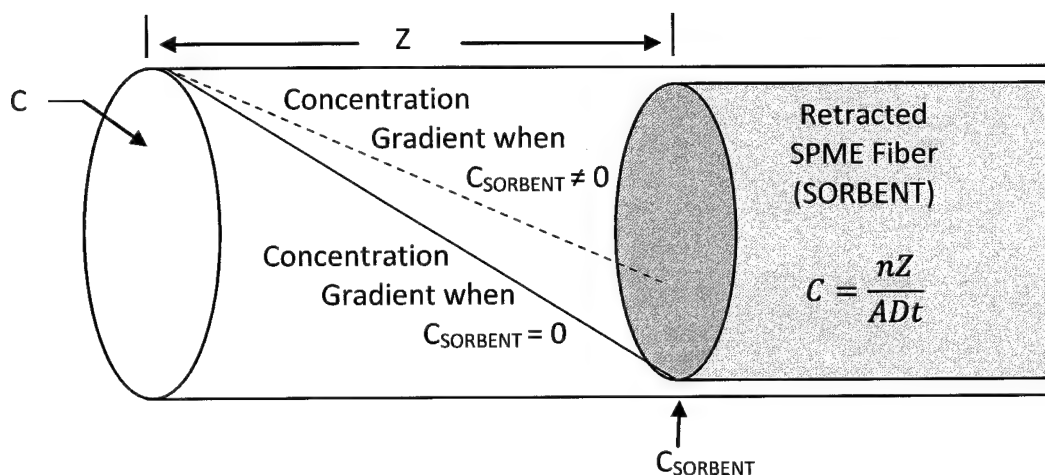


Figure 1. Passive fiber-retracted SPME

Used for quantitative sampling with Fick's first law of diffusion. Variables seen in diagram are as follows: C = TWA concentration of the target analyte; t = sampling time; Z = diffusion path length; A = the cross-sectional area of the needle; D = diffusion coefficient of the target analyte; n = amount of analyte extracted by the fiber.

Needle Trap Device (NTD)

Sampling with a needle trap device (NTD) is not a microextraction technique, but may be compared to a typical sorbent sampling approach – although on a much smaller scale. If a few mg of sorbent material are immobilized within a thin needle, analytes may be exhaustively extracted from a finite (relatively small) volume of air passed through the needle. The use of very small quantities of sorbent packed in a needle allows introduction of the NTD into a standard GC injection port for thermal desorption of trapped analytes, eliminating the need for solvent desorption. The history and theory of NTD development, and example applications have been reviewed recently by Lord and Pawliszyn.⁽²⁵⁾ However, use of packed needles as analytical tools dates back to the 1970s with large Tenax-filled needles used for fragrance collection.⁽²⁶⁾ More recently in 1997, sorbent packed needles were used to preconcentrate gaseous trace organic

compounds from human breath and ambient air.⁽²⁷⁾ The term “needle trap” was patented in 2002 by Pawliszyn following a paper studying trapping of airborne particulates.^(28, 29) In 2005, quantification of volatile organic compounds (VOCs) using an NTD was validated with NIOSH method 1501 for benzene, toluene, ethylbenzene and o-xylene (BTEX).⁽³⁰⁾ An extensive NTD study was published in 2008 describing optimization parameters, performance evaluation, and application of NTDs for the analysis of a BTEX mixture from air.⁽³¹⁾ Even though NTDs have been shown to be robust analytical tools, they are still not widely used. A 2010 review by Lord, Zhan, and Pawliszyn states, “To date, needle trap technologies have not been broadly accepted as main stream analytical techniques. We see the primary impediment to this as the current limited supply of commercial devices and... Future application of needle trap technology to conducting the entire analytical method in the field is a distinct possibility”.⁽²⁵⁾

Fick's law quantitative NTD

Another advance in NTD quantitative techniques is the passive NTD. In 2008 Gong and Pawliszyn created an NTD sample method for the volatile organic compounds (VOCs) and validated it against NIOSH method 1501. They demonstrated that BTEX could be accurately quantitated without a calibration curve by using Fick's first law of diffusion. They also determined that face velocity, humidity, and temperature were all statistically insignificant. However, their sample mass loading rate ranged from 0.03-0.07 ng/min leading to sampling times in hours not minutes.⁽³²⁾ Although passive NTD has its strengths in ease of calibration, active air sampling of small volumes will be

required to collect an adequate amount of analyte mass for detection within the short durations needed for C or STEL sampling.

Benzene

The permissible exposure limits (PELs) for benzene can be found in 29 CFR 1910.1028. Employers must ensure that workers are not exposed to TWA airborne concentrations above 1 ppm over an 8-hour workday. Employers must also ensure that workers are not exposed to STEL (15 min TWA) concentrations above 5 ppm.⁽³³⁾

The Agency for Toxic Substances and Disease Registry (ATSDR) describes benzene as a colorless liquid with a sweet odor that can be detected by humans in air at 60 ppm and in water between 0.5 and 4.5 ppm. It is produced in the petroleum industry and found naturally in volcanic emissions and forest fires. It is used in the production of plastics, resins and synthetic fibers, and it ranks among the top 20 chemical volumes produced in the United States. In high-level airborne exposures (10,000-20,000 ppm), death can result in as little as 5 min from cardiovascular effects (e.g. ventricular fibrillation), but in typical industrial environments, exposures consist of lower concentrations which are associated with long-term adverse health effects such as acute myeloid leukemia (AML).⁽³⁴⁾

The Department of Health and Human Services (DHHS) reports benzene is "known to be a human carcinogen".⁽³⁵⁾ The International Agency Research on Cancer (IARC) lists benzene as "Group 1 – carcinogenic to humans".⁽³⁶⁾ The American Conference of Governmental Industrial Hygienists (ACGIH) notates benzene as "Group A1 – confirmed human carcinogen".⁽¹⁾

Methylene Chloride

The PELs for methylene chloride can be found in 29 CFR 1910.1052. Employers must ensure that workers are not exposed to TWA airborne concentrations above 25 ppm over an 8-hour workday. Employers must also ensure that workers are not exposed to STEL (15 min TWA) concentrations above 125 ppm.⁽³⁷⁾

The ATSDR describes methylene chloride as a colorless liquid with a mild sweet odor that evaporates easily and can be detected by humans in air at 200 ppm. It is a widely used industrial solvent and paint stripper that does not appear to occur naturally in the environment. Animal studies suggest that high-level airborne exposures (8,000-20,000 ppm) can lead to unconsciousness and death caused by narcosis and respiratory depression. Long term exposure has shown carcinogenicity in animals but human data is inconclusive.^(38, 39)

The Department of Health and Human Services (DHHS) reports methylene chloride is “reasonably anticipated to be a human carcinogen”.⁽³⁵⁾ The International Agency Research on Cancer (IARC) lists methylene chloride as “Group 2B – possibly carcinogenic to humans”.⁽³⁶⁾ The American Conference of Governmental Industrial Hygienists (ACGIH) notates methylene chloride as “Group A3 – confirmed animal carcinogen with unknown relevance to humans”.⁽¹⁾

The Centers for Disease Control and Prevention (CDC) recently reported in the Morbidity and Mortality Weekly Report (MMWR) that a number of deaths relating to methylene chloride exposure in bathtub refinishing. The report concluded that from

2000 to 2011 there were 13 deaths across the United States that were directly attributed to this type of exposure.⁽⁴⁰⁾

Tetrachloroethylene

The PELs for tetrachloroethylene can be found in 29 CFR 1910.1000 TABLE Z-2. Employers must ensure that workers are not exposed to TWA airborne concentrations above 100 ppm over an 8-hour workday. Employers must also ensure that workers are not exposed to C (5 min TWA) concentrations above 300 ppm in any 3 hour period.⁽⁴¹⁾

The ATSDR describes tetrachloroethylene as a nonflammable liquid at room temperature with a sharp sweet odor that be detected by humans in air at 1 ppm. It is a synthetic chemical widely used in the dry cleaning industry and can be found as low-level background (less than 1 ppb) in the air we breath and water we drink. Historically tetrachloroethylene was used as a general anesthetic and high concentrations are known to lead to unconsciousness and in some cases, death from either respiratory depression or cardiac arrhythmia induced by epinephrine sensitization. Animal studies have shown that high concentration exposures can lead to liver and kidney cancer but this has not been shown in humans.⁽⁴²⁾

The Department of Health and Human Services (DHHS) reports tetrachloroethylene is “reasonably anticipated to be a human carcinogen”.⁽³⁵⁾ The International Agency Research on Cancer (IARC) lists tetrachloroethylene as “Group 2A – probably carcinogenic to humans”.⁽³⁶⁾ The American Conference of Governmental Industrial Hygienists (ACGIH) notates tetrachloroethylene as “Group A3 – confirmed animal carcinogen with unknown relevance to humans”.⁽¹⁾

Toluene

The PELs for toluene can be found in 29 CFR 1910.1000 TABLE Z-2. Employers must ensure that workers are not exposed to TWA airborne concentrations above 200 ppm over an 8-hour workday. Employers must also ensure that workers are not exposed to C (10 min TWA) concentrations above 500 ppm.⁽⁴¹⁾

The ATSDR describes toluene as a clear, colorless liquid with a distinctive odor that can be detected by humans in air at 8 ppm and in water between 0.04 and 1 ppm. It is a widely used solvent found in industrial and consumer products ranging from gasoline to fingernail polish and cigarette smoke. Toluene occurs naturally in crude oil and the tolu tree. High-level airborne exposures can lead to lightheadedness and in cases of continued exposure due to abusive behaviors such as sniffing glue, unconsciousness and possibly death can follow. The few documented deaths occurred from various causes including cardiac arrhythmias, central nervous system depression, and asphyxiation. Long-term exposure can lead to central nervous system damage.⁽⁴³⁾

RESEARCH OBJECTIVES

The purpose of this study was to examine the usefulness of active NTD sampling for GC/FID analysis to determine airborne contaminant concentrations over short durations. Analytes amenable to trapping by a simple single-bed sorbent system for analysis on a non-polar liquid film capillary GC column were studied.

Shorter duration sampling

The primary goal was to determine if active air sampling of a small volume (10 ml) through an NTD is viable for collecting C and STEL samples. The sample duration (1 min) was significantly shorter than the 15-min charcoal tube methods currently used for C and STEL measurements. Although current regulations call for STEL measurements over 15 min, the C measurements are supposed to be nearly instantaneous.^(1, 41)

Precise and linear response for complex chemical mixture

The method was tested with a four-analyte mixture to determine if it accurately measured C or STEL concentrations via GC-FID analysis. In order for this to be achieved, the NTD needed to provide precise results with a linear response above and below the STEL/C concentrations and the GC-FID needed to have a method for calibration of the target analytes.

Stability of sampled analyte on NTD

The NTDs were tested over a period of 14 days for stability of the sampled analytes. Both refrigerated and room temperature time-courses were conducted to determine if any significant difference would be observed. Room temperature storage was chosen as a variable, as it would be logistically desired in a real world scenario to minimize the complexity of sample shipping requirements.

CHAPTER TWO: MANUSCRIPT

NEEDLE TRAP SAMPLING WITH GAS CHROMATOGRAPHY ANALYSIS TO DETERMINE SHORT TERM EXPOSURE LIMIT AND CEILING CONCENTRATIONS FOR SELECTED ORGANIC VAPORS

Simon J. Strating¹; Michael E. Stevens Jr.¹; Duvel W. White¹; Philip A. Smith^{*2,1}

¹Uniformed Services University of the Health Sciences, Department of Preventive Medicine and Biometrics, Bethesda, Maryland; ²U.S. Department of Labor – OSHA, Health Response Team, Salt Lake Technical Center, Sandy, Utah

*Corresponding author: Smith.Philip.A@dol.gov

Keywords: needle trap device, gas chromatography, flame ionization detector, air sampling, ceiling, short term exposure limit

ABSTRACT

A needle trap device (NTD) was used for rapid (60 s) quantitative sampling of short term exposure limit (STEL) and ceiling (C) concentrations using a manually operated pump to collect small volume (10 ml) vapor samples of methylene chloride, benzene, toluene, and tetrachloroethylene. Solventless introduction of chemical samples for gas chromatography (GC) analysis with flame ionization detection (FID) yielded linear results ($>0.99 R^2$) for vapor standard mixtures of the four target analytes ranging from 10% to 200% of their respective STEL and C concentrations. The NTDs showed storage stability ($>86\%$ recovery) at room temperature over a 14-day test period. Due to the brief sampling period and the avoidance of solvent dilution, the use of NTDs for STEL/C measurements can allow industrial hygienists to collect occupational and environmental samples that reflect a nearly instantaneous exposure concentration.

INTRODUCTION

A need exists to measure nearly instantaneous vapor concentrations for a number of airborne industrial hygiene chemical stressors (hazardous chemical substances) because many current methods rely on time weighted average (TWA) samples that are not rapid enough to comply with regulatory guidance. Several types of permissible exposure limit (PEL) standards other than the frequently used eight-hour time weighted average (TWA) standard have been promulgated by the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA). These include the short term exposure limit (STEL) and ceiling (C) standards. The C standard represents a level that should never be exceeded, whereas exposure greater than the TWA STEL standard averaged over 15 min is also unacceptable.⁽¹⁾ Both the C and STEL standards are based on acute toxicity.

Current methods to measure STEL and C exposures

Current methods for evaluating STEL or C compliance rely on either quantitative handheld sensors, or a sampling and analytical method that usually relies on sorbent tube sampling with solvent desorption and analysis by gas chromatography (GC). Benzene, methylene chloride, tetrachloroethylene, and toluene samples for STEL or C compliance are all currently collected on charcoal tubes to determine 15 min TWA concentrations following GC analysis with a flame ionization detector (GC-FID).⁽²⁻⁵⁾ Analysis following solvent desorption must take into account dilution by the solvent, which reduces GC/FID sensitivity for the chemical of interest. Thus, a 15 min TWA sample is collected for C standard analytes (e.g. for tetrachloroethylene and toluene)

even though the information needed is the instantaneous sample concentration. The values of collected mass for each of the four analytes studied over a 15 min period at the respective STEL or C concentrations are shown in Table 1. It would be useful to have the option for samples to detect a nearly instantaneous concentration.

Table 1. Analytes selected for study

Analyte	STEL (ppm)	C (ppm)	^A Vapor Hazard Ratio	^B Mass of Analyte (ng) Injected for Analysis, Sampling at STEL or C Concentrations Using Current Methods (Charcoal Tube and Sorbent Desorption)
Benzene	^C 5	-----	125,263	12
Methylene Chloride	^D 125	-----	2,289	326
Tetrachloroethylene	-----	^E 300	245	509
Toluene	-----	^F 500	187	942

^AVapor hazard ratio is defined per Popendorf⁽⁴⁴⁾ as $VHR = P_{\text{vapor}} \times 106 / TLV \times 760$; relevant 8-hour OSHA permissible exposure limit standards used in place of TLV, P_{vapor} = vapor pressure, mm Hg at 25 ° C

^BCalculated by considering sampling duration, volumetric sampling rate, and sample preparation dilution

^C15 min STEL, 29 CFR 1910.1028⁽³⁾

^D15 min STEL, 29 CFR 1910.1052⁽⁴⁾

^EC standard is 200 ppm, 300 ppm acceptable maximum peak above the acceptable ceiling concentration for an 8-h shift (5 min in any 3 h), 29 CFR 1910.1000 Table Z-2⁽²⁾

^FC standard is 300 ppm, 500 ppm acceptable maximum peak above the acceptable ceiling concentration for an 8-h shift (10 min), 29 CFR 1910.1000 Table Z-2⁽⁵⁾

Possible methods to measure STEL and C exposures that do not require solvent dilution

The pace of research on sampling methods using small sorbent volumes has increased since the early 1990s when solid phase microextraction (SPME) was first described.⁽⁶⁾ "Microextraction is defined as an extraction technique where the volume of the extracting phase is very small in relation to the volume of the sample, and extraction of analytes is not exhaustive. In many cases only a small fraction of the initial analyte is extracted for analysis."⁽⁷⁾ The solid phase microextraction (SPME) technique is usually employed for passive sampling, where analytes in the system being sampled passively diffuse into a thin layer of polymer material coated over a small fused silica fiber. Eventually, equilibrium may be attained between the coating material and the system being sampled where no further net analyte uptake occurs. With SPME, the overall analyte concentration in the system being sampled is not appreciably changed due to the small scale of extraction. Qualitative screening is an important practical use for SPME due to the disadvantages associated with quantitative SPME sampling: the need for calibration curves created in the same environmental conditions as the field samples⁽¹⁰⁾ and competitive displacement of low affinity volatile organic compounds (VOCs) from the surface of sample matrices when using adsorbent fibers.⁽¹¹⁾ However, Augusto *et al.* showed that SPME can be used as a rapid quantitative field sampler if a constant flow of air is passed across the fiber during sampling,⁽⁴⁵⁾ and this makes it a candidate of interest for STEL/C sampling.

Sampling with a needle trap device (NTD) is not a microextraction technique, but may be compared to a typical sorbent sampling approach – although on a much smaller

scale. If a few milligrams of sorbent material are immobilized within a thin needle, analytes may be exhaustively extracted from a finite (relatively small) volume of air passed through the needle. The use of very small quantities of sorbent packed in a needle allows introduction of the NTD into a standard GC injection port for thermal desorption of trapped analytes, eliminating the need for solvent desorption. The history and theory of NTD development, and example applications have been reviewed recently by Lord and Pawliszyn.⁽²⁵⁾

Pawliszyn's research group has demonstrated that an NTD may be used as a passive sampling device for quantitative air sampling over periods as long as 8 h.^(46, 47) For short-duration sampling needed to accurately determine C or STEL concentrations, active air sampling of only small volumes would be required. In the case of benzene at the STEL concentration of 5 ppm, a 1 mL air sample drawn through an NTD packed with suitable sorbent would result in trapping of 16 ng of benzene (assuming no breakthrough), easily detectable by thermal desorption followed by GC-FID analysis. Thus, for short duration quantitative sampling of the kind needed to determine C and STEL compliance, sampling with an NTD would appear promising. A calibrated volumetric sample collected over a very brief duration is relatively easy to obtain rapidly in the field using an NTD and a manually operated pump. As laboratory analysis of the resulting NTD sample is by thermal desorption in the heated inlet of a calibrated gas chromatograph, this provides for analysis with no sample preparation, while also avoiding the use of solvent. This latter point eliminates the expense and environmental

risks related to collection and disposal of contaminated solvent, as well as eliminates solvent background during analysis.

The purpose of this study was to examine the usefulness of active NTD sampling for GC-FID analysis to determine airborne contaminant concentrations over short durations. Analytes amenable to trapping by a simple single-bed sorbent system for analysis on a non-polar liquid film capillary GC column were desired. The four airborne industrial hygiene chemical stressors chosen for this study were: benzene and methylene chloride for which STEL standards apply; and tetrachloroethylene and toluene for which C standards apply.

MATERIALS AND METHODS

Analytes Studied

The chemical analytes chosen for this study were methylene chloride (99.9%, Fisher Scientific, Pittsburgh, PA), benzene (99%, Fisher Scientific, Pittsburgh, PA), toluene (99.8%, Fisher Scientific, Pittsburgh, PA), and tetrachloroethylene (99%, Argos Organics, Geel, Belgium).

Needle Trap Device and Pump

Pumps and NTDs were purchased from Kitagawa America, Pompton Lakes, New Jersey – a distributor for Kitagawa, Japan and Shinwa, Japan. The Kitagawa AP-20N hand pump is designed to sample 10, 50, or 100 ml volumes of air through a Shinwa NeedlEx NTD at a rate of approximately 10 ml per min. For the proposed use to measure STEL or C concentrations, the AP-20N pump was operated using a 10 ml draw

through a NeedleEx NTD. The sorbent that Shinwa provides in their NeedleEx is 6 μ l copolymer of methacrylic acid and ethylene glycol dimethacrylate.⁽⁴⁸⁾ Figure 2 shows the Kitagawa pump with NeedleEx NTD and Figure 3 shows the components of an NTD.

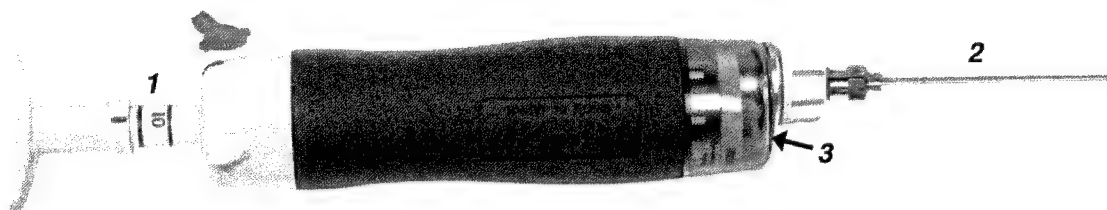


Figure 2. Gas sample pump with NTD

Kitagawa AP-20N Gas Sample Pump shown with Shinwa NeedleEx NTD. The pump handle (1) can be pulled and locked to provide 10, 50, or 100 ml sample volumes. The NTD (2) restricts the flow rate to approximately 10 ml per min. A red “pop-out” indicator (3) releases for visual confirmation that sampling is complete.

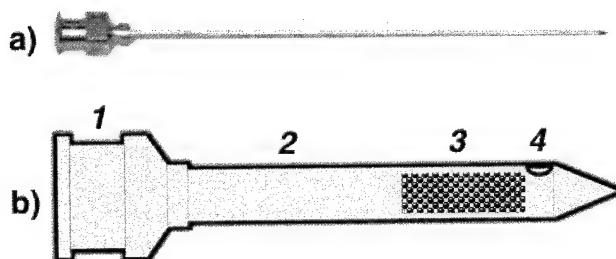


Figure 3. NeedleEx NTD and diagram

Picture of Shinwa NeedleEx NTD shown in Figure 3a and diagram of the NTD shown in Figure 3b: (1) Luer-Lok connection fitting, (2) narrow needle shaft measuring 0.7 mm O.D. by 85 mm long, (3) sorbent bed containing 6 μ l of copolymer, and (4) side-hole for sample entry. Analytes are pushed out through the same side-hole during thermal desorption in a heated GC injector.

Quantitative Standards

Vapor Standards

Tedlar® bags with a single polypropylene fitting (5 L volume, SKC, Eighty Four, PA) were prepared with a mixture of the four target analytes in known concentrations as a percentage of their respective permissible exposure limits (% nominal STEL/C) as

shown in Table 2. One day prior to each experiment, Tedlar® bags were flushed with dry nitrogen gas three times, and were then filled with 5.0 L of dry nitrogen using a large airtight syringe (1 L volume, Hamilton Chromatography, Reno, NV). Dry bags were not handled further, while bags for humid samples each received 85 µl of deionized water. The bags were then left to equilibrate overnight at 23 °C yielding 0% and 40-50% relative humidity, respectively, or 0 mg/L and 9-10 mg/L absolute humidity, respectively, as measured by water vapor tubes (1-40 mg/L, Dräger, Luebeck, Germany). One hour prior to sampling events, analyte was injected into each bag from a stock solution containing the four target analytes. For multi-hour experiments where more than one bag would be sampled, the addition of stock solution was staggered in order to maintain between 1 and 2 h of contact time between vapor standards and Tedlar® bag walls. No noticeable decreases in analyte concentrations were observed using this approach. Additionally, Sweet *et al.* demonstrated that tetrachloroethylene was found to be stable in Tedlar® bags in concentrations between 5 and 100 ppm for at least 12 h.⁽⁴⁹⁾ Each bag concentration was validated with triplicate charcoal tube samples analyzed offsite by an AIHA accredited laboratory. Unless otherwise stated, experiments utilized 50% nominal relative humidity with 100% nominal STEL/C vapor standard concentrations.

Table 2. Quantitative vapor standards

	ppm	ppm	ppm	ppm	ppm
^A Bag concentration	10%	50%	100%	150%	200%
Benzene	0.5	2.5	5	7.5	10
Methylene Chloride	12.5	62.5	125	187.5	250
Tetrachloroethylene	30	150	300	450	600
Toluene	50	250	500	750	1000
^B Solution volume used	1.9 μ l	9.4 μ l	18.9 μ l	28.3 μ l	37.7 μ l
^A Percentage of the STEL and C concentrations					
^B Stock solution mixture: 5 μ l benzene; 87 μ l methylene chloride; 333 μ l tetrachloroethylene; and 576 μ l toluene					

Liquid Standards

Creation of liquid injection standards was not straightforward due to traditional solvents co-eluting with the early eluting analytes methylene chloride and benzene. Carbon disulfide, methanol, and hexane all co-eluted with the analytes, and thus late eluting solvents were tested instead. Nonane, trimethyl phosphate (TMP), and triethyl phosphate (TEP) all eluted after the four target analytes but TMP provided the best chromatography. With TMP as the solvent, liquid injection standards were created containing nanogram (ng) equivalents of NTD samples collected at 7.5%, 50%, 100%, 150%, and 210% the STEL/C standards for the target analytes.

Gas Chromatography Analysis Method

The GC-FID instrument used in this method was an Agilent 6890N instrument with a resistively heated, low thermal mass (LTM), DB-5 column with dimensions of 0.25

mm ID, 0.25 μm d_f , and 30 m length. The GC injector was operated at 200 °C with a 4 mm gooseneck liner and a 20:1 split ratio. The column was operated at a constant pressure of 21.9 psi providing an average linear velocity of 38 cm/s. Upon introduction of sample, the carrier gas was diverted through the top of the NTD for 60 s using an automated external valve. This 1.0 min desorb eliminated all carryover and negated the need for NTD conditioning between samples as observed by a lack of response from NTD blanks run at various intervals throughout all experiments. At the start of each run, the LTM column module was held at 50 °C for 1.0 min followed by a 30 °C/min ramp to 110 °C, at which point all four analytes were observed to have eluted. The final portion of the run involved a 300 °C/min ramp to a final temperature of 250 °C with a 0.5 min hold time. Total run time was 4.0 min, followed by 3.0 min of cooling for a total of 7.0 min per run.

Needle Trap Device Performance

Breakthrough

To study breakthrough, two NTD samplers were connected in series, and a 10 ml sample was collected and analyzed for each of the five concentration vapor standard bags. Additionally, increasingly larger volumes (10 ml increments) were sampled from the 100% nominal STEL/C vapor standard bag. As mentioned earlier, the Kitagawa AP-20N pump only has increments of 10, 50, or 100 ml volumes. In order to draw increments of 10 ml, the front NTD was repeatedly sampled at this volume without analysis from the vapor standard bag while the back NTD was analyzed after each

sampling event. This allowed separate breakthrough analyses of the back NTD at cumulative volumes through the front NTD of 10, 20, 30, 40, and 50 ml.

NTD variability

Variability was tested with nine NTDs sampled in triplicate from a 100% nominal STEL/C vapor standard. Run-to-run variability on a single needle was calculated individually for each NTD using the triplicate relative standard deviation (RSD). Needle-to-needle variability was calculated from the overall RSD of the nine NTD triplicates (n=27).

Additionally, variabilities were compared between NTDs conditioned 10 days prior to use and freshly conditioned NTDs. Nine NTDs were conditioned and capped for 10 days room temperature storage (23 °C). After the 10-day storage, the nine NTDs were uncapped and used to collect 10 ml samples from a 100% nominal STEL/C vapor standard. Analysis/conditioning of each NTD was immediately followed by a second 10 ml sample collection from the 100% nominal STEL/C vapor standard. The following analysis provided the “freshly conditioned NTD” data to compare to the data collected from the samples taken 10 days after conditioning. Since the data were paired for each of the nine NTDs, two-tailed, paired, t-tests were used to compare accuracy. Precision was compared using the RSDs.

GC Liner and Humidity

Four commercially available GC injector liner designs were evaluated for quantitative run-to-run variability on a single NTD, qualitative chromatography aspects, and humidity effects of water vapor expansion in the heated injector. The evaluated

liners included: 2 mm straight, 2 mm gooseneck, 4 mm straight, and 4 mm gooseneck designs. After each liner was installed, two sets of triplicate samples were collected from 100% nominal STEL/C vapor standard bags – one triplicate sample set from a dry vapor standard bag and the other triplicate sample set from a humid vapor standard bag. Quantitative run-to-run variability was evaluated using RSD comparisons. Chromatography quality and humidity effects were evaluated visually with overlaid chromatograms.

Linearity

The five vapor standard concentrations were tested for linearity with triplicate NTD samples drawn and analyzed at each concentration. The four target analytes were sampled and analyzed together as part of each vapor standard concentration. This yielded four sets of 15 data points – one set for each target analyte. Each target analyte set was then plotted separately and evaluated for linear regression fit using R^2 values.

Liquid injection calibration curve

The five liquid standard concentrations were tested for linearity with triplicate 1.0 μ l liquid injections analyzed at each concentration. The four target analytes were analyzed together as part of each liquid standard concentration. Like the NTD vapor samples described above, this yielded four sets of 15 data points – one set for each target analyte. Each target analyte set was then plotted separately and evaluated for linear regression fit using R^2 values. The liquid standard plots (ng vs FID response) were compared to the vapor standard plots (ng vs FID response) to examine the quantitative

relationship between them in order to utilize subsequent liquid calibration curves to quantify subsequent unknown vapor samples.

Stability time-course

Two 14-day stability time-course studies were conducted on NTD samples drawn from a 100% nominal STEL/C vapor standard. One set of NTD sample was stored refrigerated (4 °C) and the other set of samples was stored at room temperature (23 °C). Nine NTDs were used for each time-course with all nine being analyzed on “day 0” followed by a second sample drawn for time-course storage. At “day 1”: NTDs 1, 2, and 3 were analyzed and compare to the values from “day 0” NTDs 1, 2, and 3. Then at “day 7”: NTDs 4, 5 and 6 were analyzed and compare to the values from “day 0” NTDs 4, 5, and 6. Finally at “day 14”: NTDs 7, 8, and 9 were analyzed and compared to the values from “day 0” NTDs 7, 8, and 9.

RESULTS AND DISCUSSION

Breakthrough

No breakthrough was observed in any of the 10 ml samples collected and analyzed from 10% to 200% nominal STEL/C vapor standard bags, as demonstrated by a lack of detectable analyte on the second NTD placed behind the first. In larger volume samples (greater than 10 mL sample volume) from the 100% nominal STEL/C vapor standard, breakthrough was observed for methylene chloride at 20 ml sample volume; then toluene at 30 ml sample volume; and finally all four analytes at 50 ml sample volume. Although toluene was sampled at its 500 ppm C and methylene chloride was

sampled at its lower 125 ppm STEL, it was not surprising to observe methylene chloride as the first analyte to breakthrough since OSHA method 59 recommends three charcoal tubes in series to prevent breakthrough during methylene chloride sampling. OSHA method 59 also describes that both humidity and additional solvents increase methylene chloride breakthrough in charcoal tubes.⁽⁴⁾ Figure 4 shows breakthrough analysis for sample volumes ranging from 10 ml to 40 ml.

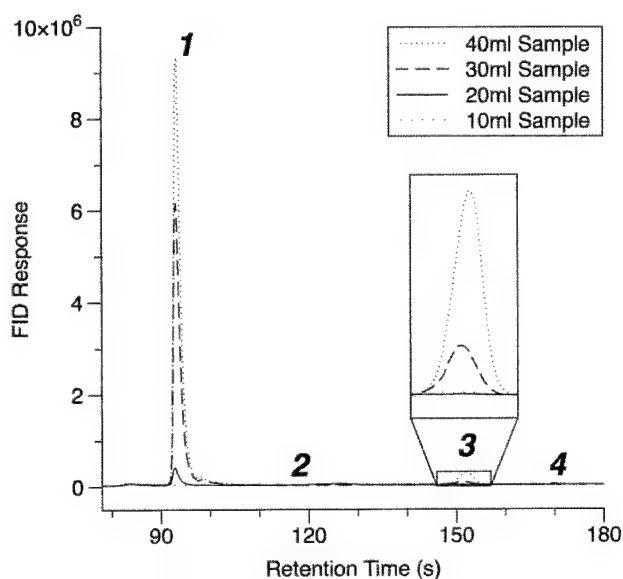


Figure 4. NTD breakthrough

GC-FID chromatograms resulting from analysis of a second NTD in series to capture analyte breaking through an NTD used to sample a Tedlar® bag (humid – 100% STEL/C nominal vapor standard concentrations): 125 ppm methylene chloride (peak **1**); 5 ppm benzene (peak **2**); 500 ppm toluene (peak **3**); and 300 ppm tetrachloroethylene (peak **4**). All chromatograms are magnified for peak **3**. The lightly dotted 10 ml sample volume chromatogram shows no FID response for any of the analytes. The solid 20 ml sample volume chromatogram shows a slight FID response for methylene chloride, indicating the beginning of breakthrough. The dashed 30 ml sample volume chromatogram shows more pronounced breakthrough of methylene chloride and slight breakthrough toluene. The dotted 40 ml sample volume chromatogram shows increased breakthrough of methylene chloride and toluene. Peaks **2** and **4** do not show evidence of breakthrough until 50 ml samples (not shown) were collected.

NTD variability

In preliminary studies sampling conducted with a single NeedlEx NTD produced highly repeatable results, whereas sampling conducted with multiple NeedlEx NTDs was slightly less reproducible. In a study of nine NTDs each sampled in triplicate these previous observations were quantified. Run-to-run variability on a single needle ranged from 1% to 5% RSD while needle-to-needle variability was 5% RSD for three of the analytes and 10% RSD for methylene chloride. Figure 5 shows a graphical representation to the variabilities with run-to-run variability of each needle represented by error bars showing the RSD and needle-to-needle variability represented by the y-axis showing differences for each NTD from the overall mean. The bar chart was useful for quick visual evaluation of the performance of each NTD when compared to another but the RSDs mentioned above give the best overall needle-to-needle statistical evaluation. For example, comparing methylene chloride results from triplicate samples on NTD #2 to triplicate samples on NTD #8 yields the largest needle-to-needle span of 27% but the methylene chloride needle-to-needle RSD was 10% when all nine NTDs were accounted for statistically. Since run-to-run variability on a single needle was lower than needle-to-needle variability, it may be prudent to follow any field sample STEL/C analysis with a known 100% STEL/C sample analysis on the same NTD. Field samples were not analyzed in the scope of this study but in future studies, especially those containing methylene chloride, post sampling correction may be needed.

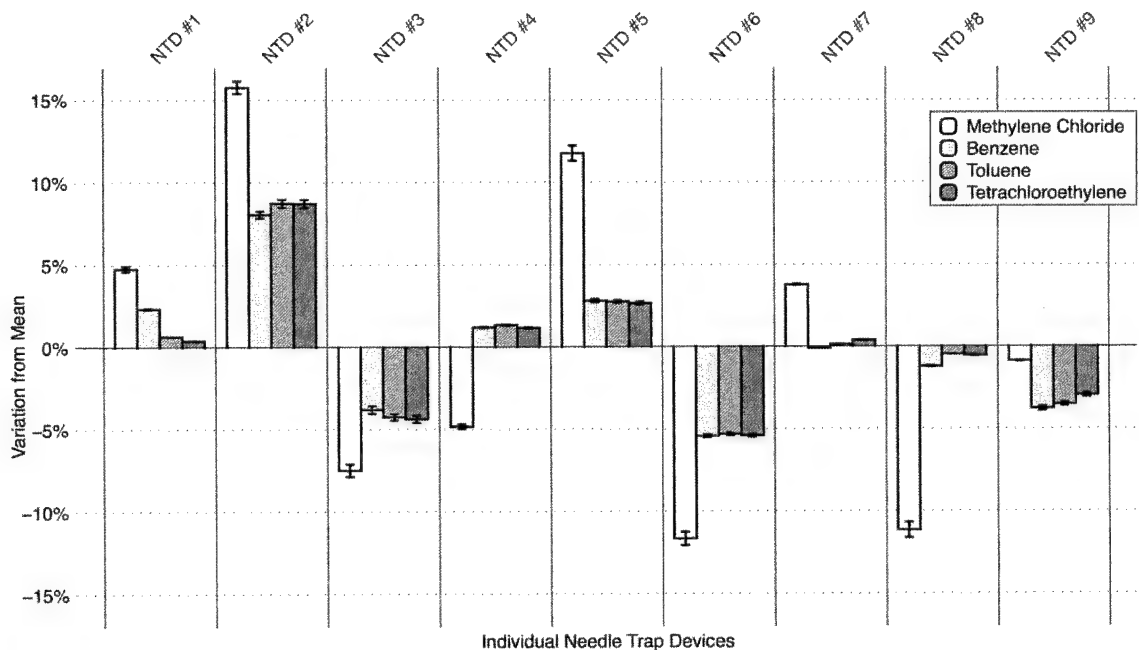


Figure 5. NTD variability

Bar graph represents 9 NTDs each sampled in triplicate from a Tedlar® bag (humid – 100% STEL/C nominal vapor standard concentrations): methylene chloride (white bars); benzene (light gray bars); toluene (gray bars); and tetrachloroethylene (dark gray bars). The X-axis shows the 4 separate analytes on each of the 9 individual NTDs. The Y-axis represents the NTD needle-to-needle variability by showing the difference of each triplicate NTD average from the overall average of all 27 samples. The error bars show run-to-run variability on a single needle via that NTD's triplicate RSD.

In addition to the above tested variabilities, leaving NTDs uncapped was noted to result in greater variability if the NTD was not conditioned prior to collecting a new sample. The accuracy and precision of 10-day capped vs fresh NTDs were compared using a two-tailed, paired, t-tests as shown in Figure 6. The t-test failed to show a statistical difference between 10-day capped and fresh NTDs at a p-value of 0.05. Additionally, the RSDs were not notably different from each other as shown by the error bars in Figure 6.

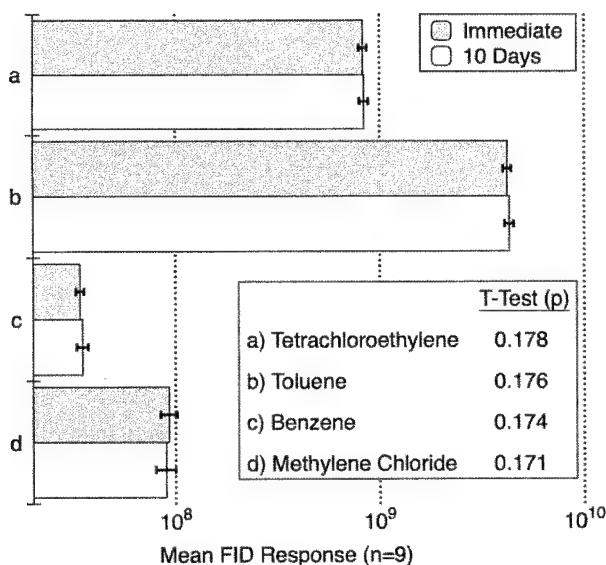


Figure 6. NTD conditioning

Following conditioning, NTD sampling results were compared between NTDs immediately used and NTDs used after 10 days storage. With 95% confidence in a paired, two-tailed t-test the analyte recoveries of the 9 NTDs compared failed to show statistical difference for any of the four target analytes. Notable differences in the RSDs (error bars) were also not observed.

GC Liner and Humidity

During the early stages of the work described in this paper, a 2 mm straight liner was used in the GC-FID because the volume of a 0.75 mm liner designed for SPME was thought to be too small to allow for vapor expansion, and a 4 mm liner designed for liquid injection was thought to be too large for rapid analyte transfer during thermal desorption. The NeedlEx NTD instructions called for a 10 s NTD heating delay between insertion of the NTD into the GC injector and pushing an inert gas through the NTD to achieve flow assisted thermal desorption.⁽⁵⁰⁾ However, the four target analytes all exhibited peak doubling with this approach. The peak doubling was thought to be caused by an initial thermal expansion peak followed by a second flow-assisted peak. To eliminate the extra peak a carrier gas bypass valve was used to allow simultaneous NTD

insertion and gas flow across the NTD. Chromatography of the four target analytes improved so that the peak doubling was only observed at the apex of peaks. In order to eliminate the double apex, the GC injector split ratio was increased from 1:10 to 1:20 and flow was decreased from 2.0 ml per min to 1.0 ml per min in order to maintain the same flow rate through the NTD during carrier gas bypass. This change lessened the apex peak doubling, leaving only a fronting peak shoulder as shown in Figure 7a. However, samples collected from humid air had a slight increase in the fronting shoulder (e.g. the toluene peak in Figure 7a). In an attempt to completely eliminate peak shoulders and humidity effects, the 2 mm straight injector liner was subsequently replaced by a 4 mm straight liner, as well as a 2 mm and 4 mm gooseneck liner, respectively. Use of the 4 mm straight liner eliminated fronting peak shoulders but had a greater loss of chromatographic resolution apparently due to slower analyte transfer caused by the larger volume of this liner. Figure 7b shows that the 2 mm gooseneck liner improved the chromatography peak sharpness and reduced the fronting peak shoulder observed with the 2 mm straight liner. Figure 7c shows that the 4 mm gooseneck liner completely eliminates fronting peak shoulders with minimal loss of peak sharpness. The relative standard deviation (RSD) for replicate samples of the four target analytes decreased as well from 4-7% RSD for the 2 mm liners to 1-2% RSD using the 4 mm gooseneck liner.

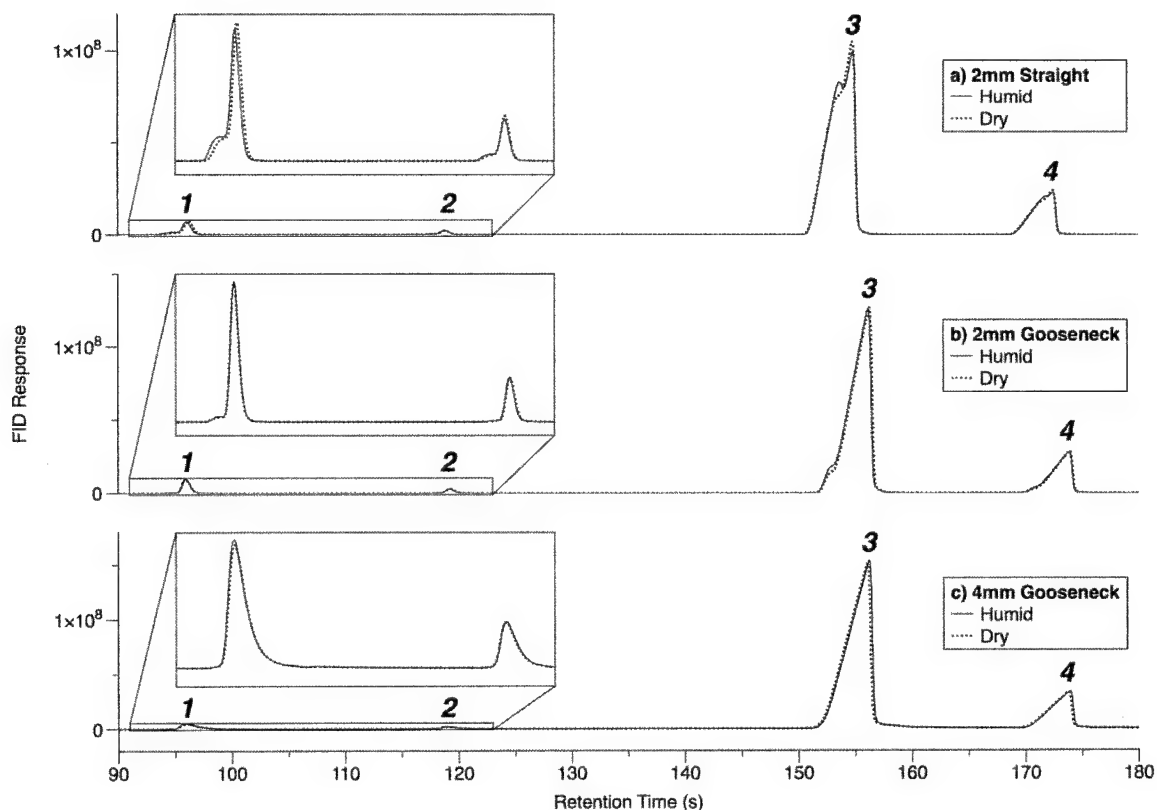


Figure 7. GC injector liner and humidity effect

GC-FID chromatograms resulting from 10 ml NTD samples drawn from both humid and dry Tedlar® bags (100% STEL/C nominal vapor standard concentrations): methylene chloride (peak **1**); benzene (peak **2**); toluene (peak **3**); and tetrachloroethylene (peak **4**). All chromatograms are magnified for peaks **1** and **2**. Figure 7a shows a slight humidity effect (larger fronting peak shoulders) in a chromatogram comparison of humid and dry samples introduced into a 2 mm straight liner (RSDs ranging from 3.5% to 5.9%). Figure 7b shows reduced fronting peak shoulder size and humidity effect in a comparison of humid and dry samples introduced into a 2 mm gooseneck liner (RSDs ranging from 5.4% to 6.7%). Figure 7c shows elimination of fronting peak shoulders and humidity effect in a comparison of humid and dry samples introduced into a 4 mm gooseneck liner (RSDs ranging from 0.3% to 2.2%). Amplified fronting observed for toluene and tetrachloroethylene are related to the relatively large concentrations of these analytes (e.g. the toluene C concentration is two orders of magnitude higher than the benzene STEL concentration).

Linearity

Use of a single NTD to sample the five vapor standard bag concentrations yielded R^2 values greater than 0.99 for all four target analytes as seen in Figures 8a, 8b, 8c, and

8d. Each of the five concentrations were sampled in triplicate and all RSDs were below 4% as seen in the error bars in Figures 8a, 8b, 8c, and 8d.

Liquid Injection Calibration Curve

Using 1 μ l liquid injections from the five liquid standard concentrations yielded R^2 values of 0.99 for three target analytes and 0.98 for benzene as seen in Figures 8a, 8b, 8c, and 8d. However, the liquid injection curve slopes did not match the vapor standard curve slopes so a correction equation was needed: $\Delta Y = (m_{NTD} - m_{liquid}) X + (b_{NTD} - b_{liquid})$. This equation is instrument-dependent but once it has been determined it can then be used to reconstruct an NTD calibration curve on subsequent days with only liquid standards. This was demonstrated with a single expected concentration gas mixture of the four target analytes at 100% nominal STEL/C. The reconstructed calibration curve predicted the correct NTD bag sample concentrations within 5% to 9% for all target analytes except methylene chloride, which was within 15%.

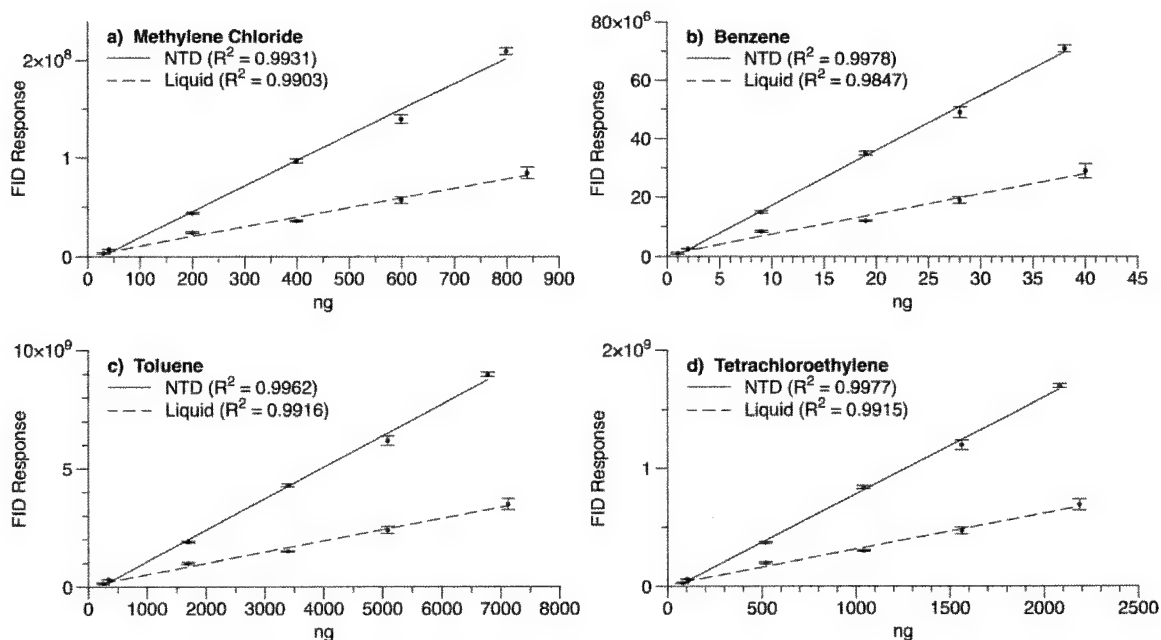


Figure 8. Linearity and liquid calibration

Linear regression curves of NTD samples from multiple concentration gas mixtures (10%, 50%, 100%, 150%, and 200% the STEL/C concentrations) were compared to liquid injection dilutions containing ng equivalents of the NTD samples. Since the liquid injection curve slopes did not match the NTD curve slopes, the correction equation, $\Delta Y = (m_{NTD} - m_{liquid}) X + (b_{NTD} - b_{liquid})$, was used.

Stability Time-Course

Stability of samples during shipment is important for a field method that requires off-site analysis so the NTDs were tested for storage stability over time. Figure 9 shows no notable difference between storage at 4 °C and storage at 23 °C. At room temperature, the NTDs retained an average of greater than 86% of the sampled target analytes for 14 days.

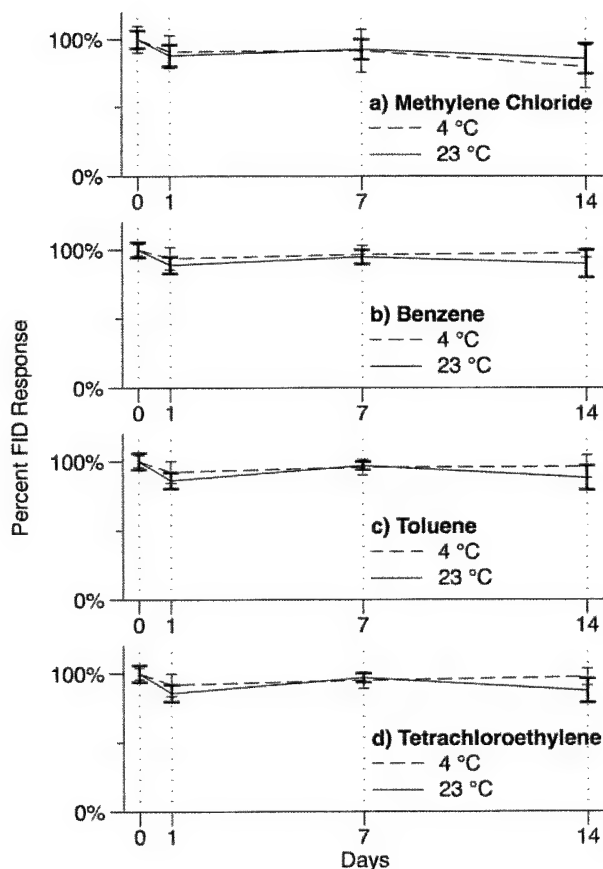


Figure 9. NTD stability time-course

NTD storage stability of the four target analytes over 14 days at 4 °C and 23 °C yielded the following (4 °C & 23 °C) recoveries at 14 days: 80% & 86% methylene chloride (Figure 9a); 98% & 90% benzene (Figure 9b); 96% & 88% toluene (Figure 9c); and 97% & 87% tetrachloroethylene (Figure 9d).

CONCLUSION

The ability to rapidly sample target chemical vapors with an NTD was demonstrated for both C and STEL analysis of airborne industrial hygiene chemical stressors. The quantitative GC-FID results were highly repeatable and linear from 10% to 200% of the STEL/C concentrations. In addition, samples remained stable after collection on the NTD for 14 days at room temperature.

This NTD STEL/C method uses a hand pump, which does not require batteries and is simple to operate in the field. It also reduces current collection methods from 15 min to 1 min with low sampling volumes of only 10 ml. Additionally, solventless sample extraction eliminates the need for solvents like carbon disulfide. This new rapid quantitative use of the NTD has the potential to improve the ability of industrial hygienists to collect occupational and environmental samples that reflect a nearly instantaneous exposure concentration.

A limitation of the NTD STEL/C method is cost of the NTDs. However, the reusability of NTD samplers (25~30 field uses)⁽⁵⁰⁾ make the operating costs comparable to current non-reusable charcoal tube methods.

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CHAPTER THREE: CONCLUSION

DISCUSSION

The ability to rapidly sample target chemical vapors with an NTD was demonstrated for both C and STEL analysis of airborne industrial hygiene chemical stressors. The quantitative GC-FID results were highly repeatable and linear from 10% to 200% of the STEL/C concentrations. In addition, samples remained stable after collection on the NTD for 14 days at room temperature.

One limitation of the NTD STEL/C method is cost of the NTDs. However, the reusability of NTD samplers (25~30 field uses)⁽⁵⁰⁾ make the operating costs comparable to current non-reusable charcoal tube methods. Another limitation is the design of the NeedleEx NTD: the side-hole sample entry/exit port nicks the injector septum during each insertion, which leads to faster than normal septum degradation and occasionally clogged NTDs. Additionally, the copolymer sorbent bed can only be heated to 200 °C in the injector, which leads to injector discrimination of less volatile larger chemicals, which require longer flow assisted thermal desorption times. The greatest limitation of this NTD STEL/C method is the need for a carrier gas bypass valve to be retrofitted on the GC-FID as shown by the diagram in Figure 10. The market for NTDs has not become ubiquitous enough for GC instruments to offer commercial products for flow assisted NTD desorption. The electronic valve used in this research was custom built by Torion® Technologies Inc.⁽⁵¹⁾

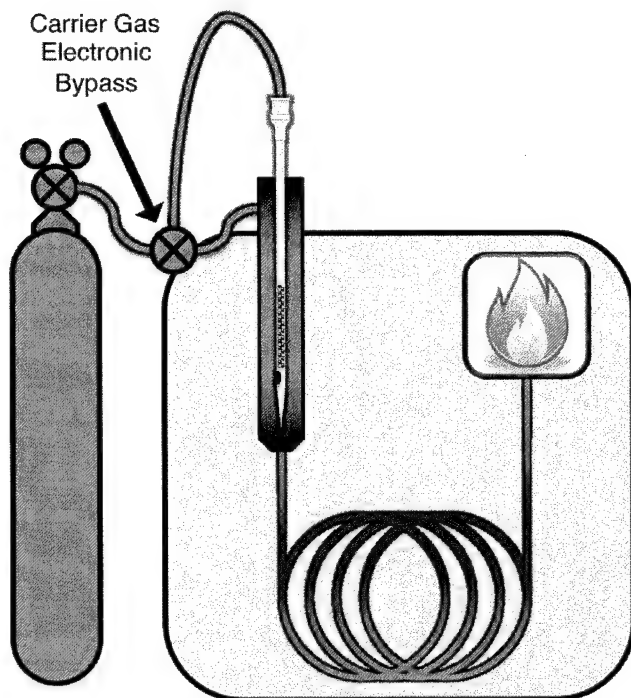


Figure 10. GC-FID with electronic carrier gas bypass

Electronic valve spliced into GC-FID carrier gas line to provide flow assisted desorption of the NTD in the heated injector port.

IMPLICATIONS

This NTD STEL/C method uses a hand pump, which does not require batteries and is simple to operate in the field. It also reduces current collection methods from 15 min to 1 min with low sampling volumes of only 10 ml. Additionally, solventless sample extraction eliminates the need for solvents like carbon disulfide. This new rapid quantitative use of the NTD has the potential to improve the ability of industrial hygienists to collect occupational and environmental samples that reflect a nearly instantaneous exposure concentration.

Additionally, NTD field sampling has great military potential. US Army Environmental Science and Engineering Officers (ESEOs) are expected to provide basic

Industrial Hygiene (IH) support under numerous conditions Outside of Contiguous United States (OCONUS) and to a lesser extent in Contiguous United States (CONUS). This IH support often involves presenting Commanders with risk assessments of Indoor Air Quality (IAQ) for buildings already occupied or buildings planned for occupation. The majority of ESEOs are junior officers (190 Company Grades, 52 Majors, and 52 more senior Field Grades) and many have only rudimentary IH training. In fact, there are only 3 Certified Industrial Hygienists (CIHs) out of the 294 Active Duty Army ESEOs.⁽⁵²⁾ This lack of IH experience can leave ESEOs wondering if they should conduct air sampling, what type of media they should use, and how many samples they should collect. The rapid light weight sampling capabilities of an NTD paired with the simplicity of a manual hand pump would allow the ESEO or any newly trained Soldier to collect multiple field samples in a short duration and transport those samples without noticeable bulk or weight. This could provide simple yet definitive quantitative profiles of chemicals affecting IAQ. With NTDs and a hand pump, ESEOs could be equipped with all the required information to provide IAQ risk assessments with “high confidence level”.⁽⁵³⁾

FUTURE RESEARCH

The ACGIH TLV lists 161 chemicals with STEL or C concentrations,⁽¹⁾ and each of these could benefit from a quicker sampling method and simple solventless sample preparation/introduction in the laboratory. Additionally, chemical warfare agent (CWA) quantification could be greatly improved with the rapid capabilities of the NTD – including shorter durations spent in the “hot zone” by CWA response personnel or the ability of CWA personnel to sample more areas of the “hot zone” in a given timeframe.

Another research project that does not pertain to STEL/C measurement is on-site rapid quantitative analysis. Portable gas chromatography – mass spectrometry (GC-MS) could be paired with an NTD to provide person-portable, on-site rapid quantification. Figure 11 shows a pilot study of toxic industrial chemicals (TICs) and CWA surrogates in the low ppb concentration range which were quantitatively sampled on a thermal desorption (TD) tube and then thermally transferred to an NTD preconcentrator for analysis on a person-portable Torion® TRIDION™-9 GC-MS (pre-production model). A current USUHS Ph.D. candidate will likely continue this research.

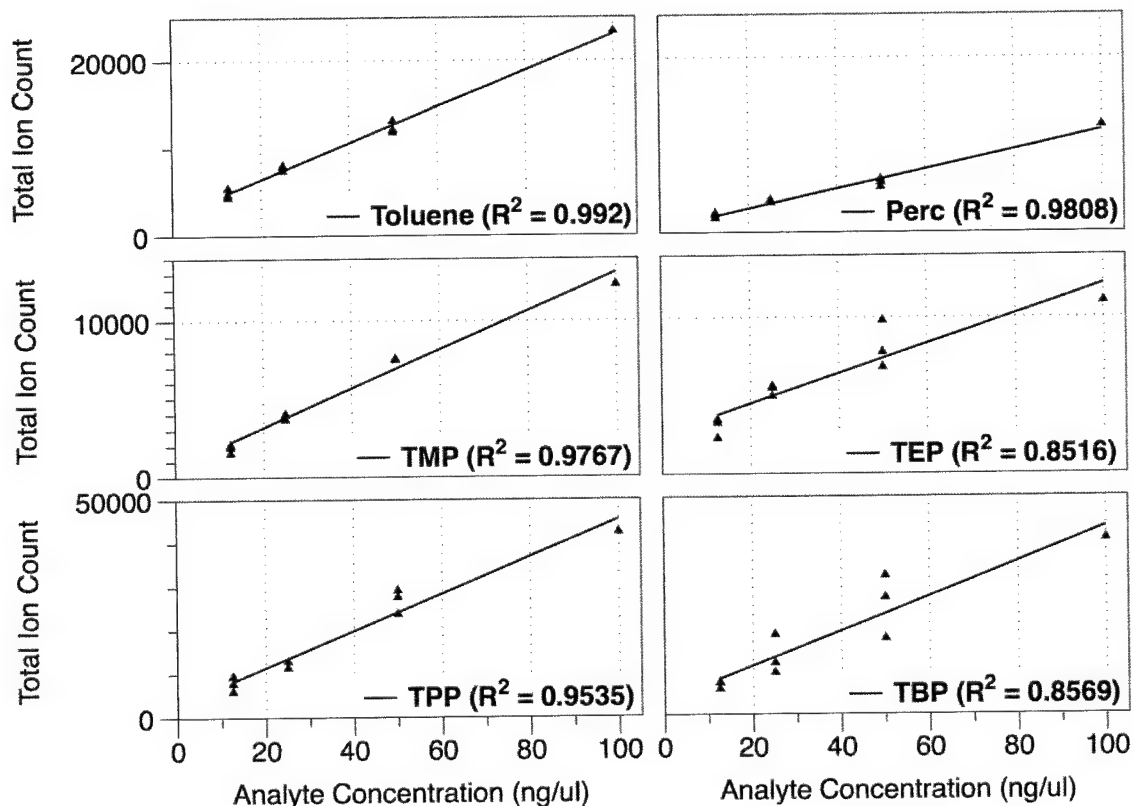


Figure 11. Person-portable GC-MS quantitation using an NTD

Pilot study of TICs (Toluene and Perchloroethylene) and CWA surrogates (Trimethyl Phosphate, Triethyl Phosphate, Tripropyl Phosphate, and Tributyl Phosphate) in the low ppb range being quantitatively sampled on a TD tube and then thermally transferred to an NTD preconcentrator for analysis on a person-portable Torion® TRIDION™-9 preproduction GC-MS. Liquid stock solutions of the target analytes were mixed at four concentrations then loaded 1 µl at a time onto a TD tubes. The analytes were then transferred from TD tubes to NTD via a compact heated transfer module. Then the NTD was quantitatively analyzed on the person-portable GC-MS. The y-axis is the total ion count peak area for each sample. The x-axis is concentration of liquid stock solution loaded onto the TD tubes.

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